

**UNITED STATES PATENT APPLICATION**  
**OF**  
**LUC GOURLAOUEN AND HENRI SAMAIN**  
**FOR**  
**COMPOSITION FOR DYEING HUMAN KERATIN MATERIALS, COMPRISING AT**  
**LEAST ONE FLUORESCENT DYE AND AT LEAST ONE ASSOCIATIVE POLYMER,**  
**PROCESS THEREFOR AND USE THEREOF**

[001] This application claims benefit of U.S. Provisional Application No. 60/468,080, filed May 6, 2003.

[002] Disclosed herein are compositions comprising at least one fluorescent dye and at least one associative polymer, and the processes and a device for using the composition. Further disclosed herein is the use of the composition comprising at least one fluorescent dye and at least one associative polymer to dye with a lightening effect human keratin materials, for example, keratin fibers such as artificially dyed or pigmented hair, and dark skin.

[003] It is common for individuals with dark skin to wish to lighten their skin and for this purpose to use cosmetic or dermatological compositions containing bleaching agents.

[004] The substances most commonly used as bleaching agents are hydroquinone and its derivatives, kojic acid and its derivatives, azelaic acid, and arbutin and its derivatives, alone or in combination with other active agents.

[005] However, these agents have some drawbacks. For example, they need to be used for a long time and in large amounts in order to obtain a bleaching effect on the skin. No immediate effect is observed upon applying compositions comprising them.

[006] In addition, hydroquinone and its derivatives are used in an amount that is effective to produce a visible bleaching effect. For example, hydroquinone is known for its cytotoxicity towards melanocyte.

[007] Moreover, kojic acid and its derivatives have the drawback of being expensive and consequently of not being able to be used in large amounts in products for commercial mass distribution.

[008] There is thus still a need for cosmetic compositions that allow a lighter, uniform, homogeneous skin tone of natural appearance to be obtained, and at the same time, these compositions can have satisfactory transparency after application to the skin.

[009] In the field of haircare, there are mainly two types of hair dyeing.

[010] The first type is semi-permanent dyeing or direct dyeing, which uses dyes capable of giving the hair's natural color a more or less pronounced modification that can withstand shampooing several times. These dyes are known as direct dyes and may be used in two different ways. The colorations may be performed by applying a composition comprising at least one direct dye directly to the keratin fibers, or by applying a mixture, prepared extemporaneously, of a composition comprising at least one direct dye with a composition comprising at least one oxidizing bleaching agent, which is, for example, aqueous hydrogen peroxide solution. Such a process is then termed "lightening direct dyeing."

[011] The second type is permanent dyeing or oxidation dyeing. This can be performed with "oxidation" dye precursors, which are colorless or weakly colored compounds which, once mixed with oxidizing products, at the time of use, can give rise to colored compounds and dyes via a process of oxidative condensation. At least one direct dye is often used in combination with the oxidation bases and couplers in order to neutralize or attenuate the shades with too much of a red, orange or golden glint or, on the contrary, to accentuate these red, orange or golden glints.

[012] Among the available direct dyes, nitrobenzene direct dyes are not sufficiently strong, and indoamines, quinone dyes and natural dyes may have low affinity for keratin fibers and consequently lead to colorations that may not be sufficiently fast with respect to the various treatments to which the keratin fibers may be subjected, such as shampooing.

[013] In addition, there is a need to obtain a lightening effect on human keratin fibers. This lightening has conventionally been obtained via a process of bleaching the melanins of the hair via an oxidizing system generally comprising hydrogen peroxide optionally combined with persalts. This bleaching system may have the drawback of degrading the keratin fibers and of impairing their cosmetic properties.

[014] Therefore, there is still a need to solve at least one of the problems mentioned above, and, for example, to provide a composition that can have good dyeing affinity for keratin materials such as keratin fibers, good resistance properties with respect to external agents, such as with respect to shampooing, and that can also make it possible to obtain lightening without impairing the treated material, such as the keratin fibers.

[015] It has thus been found, surprisingly and unexpectedly, that the use of fluorescent dyes, such as those in the orange range, in the presence of particular associative polymers, can satisfy at least one of these needs.

[016] Disclosed herein is thus a composition comprising, in a cosmetically acceptable medium, at least one fluorescent dye that is soluble in the medium and at least one associative polymer chosen from associative polyurethane derivatives, associative cellulose derivatives, associative polyvinyl lactam derivatives and associative unsaturated polyacid derivatives; provided that the composition does not comprise, as a fluorescent agent, 2-[2-(4-dialkylamino)phenylethenyl]-1-alkylpyridinium wherein the alkyl radical of the pyridinium nucleus is a methyl or ethyl radical, the alkyl radical of the benzene nucleus is a methyl radical, and the counterion is a halide.

[017] Further disclosed herein is a process for dyeing human keratin fibers with a lightening effect, comprising:

- a) applying to the keratin fibers the composition disclosed herein for a time

that is sufficient to develop a desired coloration and lightening,

- b) optionally rinsing the keratin fibers,
- c) optionally washing the keratin fibers with shampoo and optionally rinsing the keratin fibers, and
- d) drying or leaving the keratin fibers to dry.

[018] Further disclosed herein is the use of a composition for dyeing human keratin materials with a lightening effect, comprising, in a cosmetically acceptable medium, at least one fluorescent dye that is soluble in the medium, and at least one associative polymer chosen from associative polyurethane derivatives, associative cellulose derivatives, associative polyvinyl lactam derivatives and associative unsaturated polyacid derivatives.

[019] Further disclosed herein is a multi-compartment device for dyeing and lightening keratin fibers, comprising at least one compartment comprising the composition disclosed herein, and at least one other compartment comprising a composition comprising at least one oxidizing agent.

[020] The compositions disclosed herein can, for example, allow better fixing of the fluorescent dye onto the keratin materials, which is reflected by an increased fluorescent effect and a lightening effect that is greater than that obtained with the fluorescent dye used alone.

[021] Better resistance of the result with respect to washing or shampooing can also be obtained.

[022] However, other characteristics and advantages of the present disclosure will emerge more clearly on reading the description and the examples that follow.

[023] Unless otherwise indicated, the limits of the ranges of values that are given in the description are included in these ranges.

[024] As has been mentioned previously, the composition disclosed herein comprises at least one fluorescent dye and at least one associative polymer chosen from associative polyurethane derivatives, associative cellulose derivatives, associative polyvinylactam derivatives and associative unsaturated polyacid derivatives.

[025] The associative polymers are hydrophilic polymers capable, in an aqueous medium, of reversibly combining together or with other molecules.

[026] Their chemical structure, for example, may comprise at least one hydrophilic region and at least one hydrophobic region.

[027] The term "hydrophobic group" means a radical or polymer comprising at least one chain chosen from saturated and unsaturated, linear and branched hydrocarbon-based chains.

[028] When it denotes a hydrocarbon-based radical, the hydrophobic group comprises at least 10 carbon atoms, such as from 10 to 30 carbon atoms, further such as from 12 to 30 carbon atoms, and even further such as from 18 to 30 carbon atoms.

[029] In one embodiment, the hydrocarbon-based group is derived from a monofunctional compound.

[030] By way of example, the hydrophobic group may be derived from a fatty alcohol such as stearyl alcohol, dodecyl alcohol and decyl alcohol. It may also be a hydrocarbon-based polymer, for example, polybutadiene.

[031] The associative polymers present in the composition disclosed herein may be of nonionic, anionic, cationic or amphoteric nature.

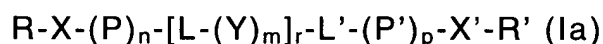
[032] Among the associative polyurethane derivatives that may be mentioned are, for example, anionic copolymers obtained by polymerization of:

- from 20% to 70% by weight of an  $\alpha,\beta$ -monoethylenically unsaturated carboxylic acid,

- from 20% to 80% by weight of a non-surfactant  $\alpha,\beta$ -monoethylenically unsaturated monomer different from the preceding monomer, and
- from 0.5% to 60% by weight of a nonionic monourethane, which is the product of reaction of a monohydroxylated surfactant with a monoethylenically unsaturated monoisocyanate.

[033] Such derivatives are described, for example, in European document EP 173 109, such as in Example 3. In one embodiment, this polymer is a methacrylic acid/methyl acrylate/ethoxylated (40 EO) behenyl alcohol dimethyl-meta-isopropenylbenzylisocyanate terpolymer as an aqueous 25% dispersion. This product is sold under the reference Viscophobe DB1000 by the company Amerchol.

[034] Mention may also be made of the cationic associative polyurethanes whose family has been described, for example, in French patent application FR 00/09609. It may be represented, for example, by the general formula (Ia) below:



wherein:

[035] R and R', which may be identical or different, are each chosen from hydrophobic groups and a hydrogen atom;

[036] X and X', which may be identical or different, are each chosen from groups comprising at least one amine functional group optionally bearing at least one hydrophobic group, and a group L";

[037] L, L' and L", which may be identical or different, are each chosen from groups derived from a diisocyanate;

[038] P and P', which may be identical or different, are each chosen from groups comprising at least one amine functional group optionally bearing at least one hydrophobic group;

[039] Y is chosen from hydrophilic groups;

[040] r is an integer ranging from 1 to 100, such as from 1 to 50, and further such as from 1 to 25;

[041] n, m and p, which may be identical or different, each range from 0 to 1000;

[042] provided that the molecule comprises at least one amine functional group chosen from protonated and quaternized amine functional groups and at least one hydrophobic group.

[043] In one embodiment, the only hydrophobic groups of these polyurethanes are the groups R and R' located at the chain ends.

[044] In another embodiment, the cationic associative polyurethane corresponds to the formula (Ia) described above, wherein:

[045] R and R' are each chosen from hydrophobic groups,

[046] X and X' are each a group L",

[047] n and p range from 1 to 1000, and

[048] L, L', L", P, P', Y and m have the meaning given in the above-mentioned formula (Ia).

[049] In yet another embodiment, the cationic associative polyurethane corresponds to the formula (Ia) above, wherein:

[050] R and R' are each chosen from hydrophobic groups,

[051] X and X' are each a group L", n and p are 0, and L, L', L", Y and m have the meaning given in the above-mentioned formula (Ia).

[052] The fact that n and p are 0 means that these polymers do not comprise units derived from a monomer comprising at least one amine functional group incorporated into the polymer during the polycondensation. The protonated amine functional groups of these



polyurethanes result from the hydrolysis of excess isocyanate functional groups, at the chain end, followed by alkylation of the primary amine functional groups formed with alkylating agents comprising at least one hydrophobic group, *i.e.*, compounds of the type RQ or R'Q, wherein R and R' are as defined above and Q is a leaving group such as a halide, a sulphate, etc.

[053] In yet another embodiment, the cationic associative polyurethane corresponds to the formula (Ia) above wherein:

[054] R and R' are each chosen from hydrophobic groups,

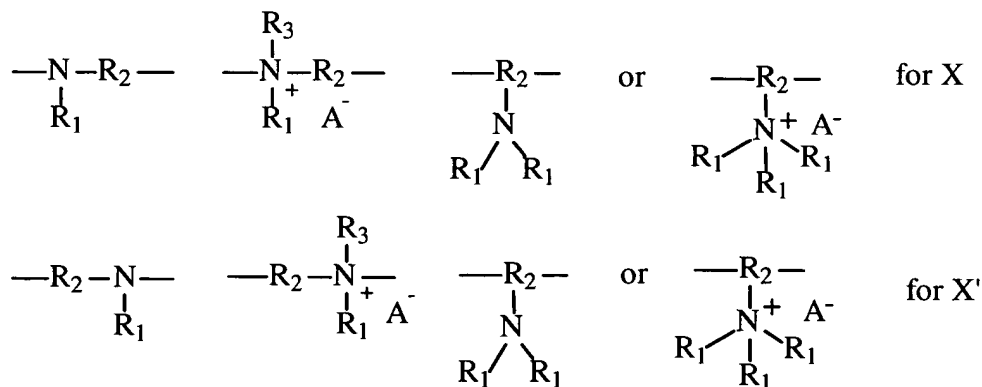
[055] X and X' are each a group comprising a quaternary amine functional group,

[056] n and p are zero, and

[057] L, L', Y and m have the meaning given in the above-mentioned formula (Ia).

[058] The number-average molecular mass of the cationic associative polyurethanes ranges, for example, from 400 to 500 000, such as from 1000 to 400 000, and further such as from 1000 to 300 000 g/mol.

[059] When at least one of X and X' is a group comprising at least one amine functional group chosen from tertiary and quaternary amine functional groups, at least one of X and X' may be a group of one of the following formulae:



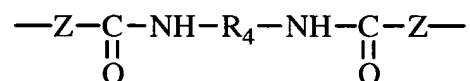
wherein:

[060]  $R_2$  is a radical chosen from linear and branched alkylene radicals comprising from 1 to 20 carbon atoms, optionally comprising at least one ring chosen from saturated and unsaturated rings, and arylene radicals, wherein at least one of the carbon atoms is possibly replaced with a hetero atom chosen from N, S, O and P;

[061]  $R_1$  and  $R_3$ , which may be identical or different, are each a radical chosen from linear and branched  $C_1$ - $C_{30}$  alkyl and alkenyl radicals, and aryl radicals, wherein at least one of the carbon atoms is possibly replaced with a hetero atom chosen from N, S, O and P;

[062]  $A^-$  is a physiologically acceptable counterion.

[063] The groups L, L' and L'' are each a group of formula:

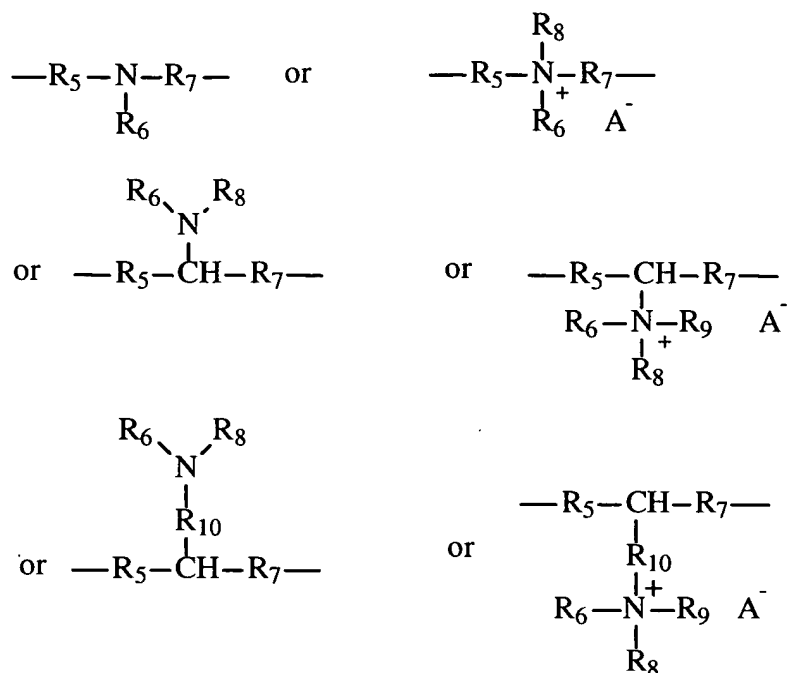


wherein:

[064] Z is -O-, -S- or -NH-; and

[065]  $R_4$  is a radical chosen from linear and branched alkylene radicals comprising from 1 to 20 carbon atoms, optionally comprising at least one ring chosen from saturated and unsaturated rings, and arylene radicals, wherein at least one of the carbon atoms is possibly replaced with a hetero atom chosen from N, S, O and P.

[066] The groups P and P' may comprise at least one amine functional group and may each be a group of at least one of the following formulae:



wherein:

[067] R<sub>5</sub> and R<sub>7</sub>, which may be identical or different, have the same meanings as R<sub>2</sub> defined above;

[068] R<sub>6</sub>, R<sub>8</sub> and R<sub>9</sub>, which may be identical or different, have the same meanings as R<sub>1</sub> and R<sub>3</sub> defined above;

[069] R<sub>10</sub> is a group chosen from linear and branched, optionally unsaturated alkylene groups possibly comprising at least one hetero atom chosen from N, O, S and P; and

[070] A<sup>-</sup> is a cosmetically acceptable counterion.

[071] With regard to the meaning of Y, the term "hydrophilic group" means a polymeric or non-polymeric water-soluble group.

[072] By way of example, when it is not a polymer, mention may be made of ethylene glycol, diethylene glycol and propylene glycol.

[073] When it is a hydrophilic polymer, in accordance with one embodiment, mention may be made, for example, of polyethers, sulphonated polyesters, sulphonated

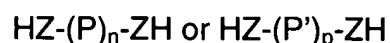
polyamides or a mixture of these polymers. The hydrophilic compound is, for example, a polyether, such as a poly(ethylene oxide) and a poly(propylene oxide).

[074] The cationic associative polyurethanes of the formula (Ia) disclosed herein may be formed from diisocyanates and from various compounds with functional groups comprising at least one labile hydrogen. The functional groups comprising at least one labile hydrogen may be chosen, for example, from alcohol, primary and secondary amine, and thiol functional groups, giving, after reaction with the diisocyanate functional groups, polyurethanes, polyureas and polythioureas, respectively. As used herein, the term "polyurethanes" includes these three types of polymers, namely polyurethanes, polyureas and polythioureas, and also copolymers thereof.

[075] A first type of compound involved in the preparation of the polyurethane of the formula (Ia) is a compound comprising at least one unit comprising at least one amine functional group. This compound may be multifunctional, for example, the compound may be difunctional, *i.e.*, in one embodiment, this compound comprises two labile hydrogen atoms borne, for example, by a hydroxyl, primary amine, secondary amine or thiol functional group. A mixture of multifunctional and difunctional compounds in which the percentage of multifunctional compounds is low may also be used.

[076] As mentioned above, this compound may comprise more than one unit comprising at least one amine functional group. In this case, it is a polymer bearing a repetition of the unit comprising at least one amine functional group.

[077] Compounds of this type may be represented by the following formula:



wherein Z, P, P', n and p are as defined above.

[078] Examples of compounds comprising at least one amine functional group that may be mentioned include N-methyldiethanolamine, N-tert-butyldiethanolamine and N-sulphoethyldiethanolamine.

[079] A second compound involved in the preparation of the polyurethane of the formula (Ia) may be a diisocyanate corresponding to the formula  $O=C=N-R_4-N=C=O$  wherein  $R_4$  is as defined above.

[080] Mention may be made, for example, of methylenediphenyl diisocyanate, methylenecyclohexane diisocyanate, isophorone diisocyanate, toluene diisocyanate, naphthalene diisocyanate, butane diisocyanate and hexane diisocyanate.

[081] A third compound that may be involved in the preparation of the polyurethane of the formula (Ia) is a hydrophobic compound intended to form the terminal hydrophobic groups of the polymer of the formula (Ia).

[082] This compound comprises at least one hydrophobic group and at least one functional group comprising a labile hydrogen, for example, a hydroxyl, primary or secondary amine, or thiol functional group.

[083] By way of example, this compound may be a fatty alcohol such as stearyl alcohol, dodecyl alcohol and decyl alcohol. When this compound comprises a polymeric chain, it may be, for example,  $\alpha$ -hydroxylated hydrogenated polybutadiene.

[084] The hydrophobic group of the polyurethane of the formula (Ia) may also result from the quaternization reaction of the tertiary amine of the compound comprising at least one tertiary amine unit. Thus, the hydrophobic group is introduced via the quaternizing agent. This quaternizing agent may be a compound of the type  $RQ$  or  $R'Q$ , wherein  $R$  and  $R'$  are as defined above and  $Q$  is a leaving group such as a halide or a sulphate, etc.

[085] The cationic associative polyurethane may also comprise at least one hydrophilic block. This block may be provided by a fourth type of compound involved in the preparation of the polymer. This compound may be multifunctional. For example, it may be difunctional. It is also possible to have a mixture of multifunctional and difunctional compounds in which the percentage of multifunctional compound is low.

[086] The functional groups comprising a labile hydrogen are chosen from alcohol, primary and secondary amine, and thiol functional groups. This compound may be a polymer terminated at the chain ends with one of these functional groups comprising a labile hydrogen.

[087] By way of example, when it is not a polymer, mention may be made of ethylene glycol, diethylene glycol and propylene glycol.

[088] When it is a hydrophilic polymer, mention may be made, for example, of polyethers, sulphonated polyesters and sulphonated polyamides, or a mixture of these polymers. The hydrophilic compound is, for example, a polyether such as a poly(ethylene oxide) or a poly(propylene oxide).

[089] The hydrophilic group termed Y in the formula (Ia) is optional. Specifically, the units comprising a quaternary amine or protonated functional group may suffice to provide the solubility or water-dispersibility required for this type of polymer in an aqueous solution.

[090] Although the presence of a hydrophilic group Y is optional, in one embodiment, the cationic associative polyurethanes disclosed herein comprise such a group.

[091] The associative polyurethane derivatives disclosed herein may also be nonionic polyether polyurethanes. For example, the polymers may comprise in their chain

both hydrophilic blocks usually of polyoxyethylenated nature and hydrophobic blocks that may be chosen from aliphatic sequences alone and cycloaliphatic and aromatic sequences.

[092] In one embodiment, these polyurethane polyethers comprise at least two hydrocarbon-based lipophilic chains comprising from 6 to 30 carbon atoms, separated by a hydrophilic block, wherein the hydrocarbon-based chains are possibly pendent chains, or chains at the end of the hydrophilic block. For example, it is possible for at least one pendent chain to be included. In addition, the polymer may comprise at least one hydrocarbon-based chain at one end or at both ends of a hydrophilic block.

[093] The polyurethane polyethers may be multiblock, such as in triblock form. Hydrophobic blocks may be at each end of the chain (for example: triblock copolymer with a hydrophilic central block) or distributed both at the ends and in the chain (for example: multiblock copolymer). These same polymers may also be graft polymers or starburst polymers.

[094] The nonionic fatty-chain polyurethane polyethers may be triblock copolymers wherein the hydrophilic block is a polyoxyethylenated chain comprising from 50 to 1000 oxyethylene groups.

[095] The nonionic polyurethane polyethers comprise a urethane linkage between the hydrophilic blocks, whence arises the name.

[096] Also included in the nonionic hydrophobic-chain polyurethane polyethers may be those in which the hydrophilic blocks are linked to the hydrophobic blocks via other chemical bonds.

[097] Examples of nonionic hydrophobic-chain polyurethane polyethers that may be used herein include Rheolate 205<sup>®</sup> comprising a urea functional group, sold by the company Rheox, or Rheolate<sup>®</sup> 208, 204 or 212, and also Acrysol RM 184<sup>®</sup>.

[098] Mention may also be made of the product Elfacos T210<sup>®</sup> comprising a C<sub>12</sub>-C<sub>14</sub> alkyl chain, and the product Elfacos T212<sup>®</sup> comprising a C<sub>18</sub> alkyl chain, from Akzo.

[099] The product DW 1206B<sup>®</sup> from Rohm & Haas comprising a C<sub>20</sub> alkyl chain and a urethane linkage, sold at a solids content of 20% in water, may also be used.

[0100] It is also possible to use solutions or dispersions of these polymers, such as in water or in aqueous-alcoholic medium. Examples of such polymers that may be mentioned are Rheolate<sup>®</sup> 255, Rheolate<sup>®</sup> 278 and Rheolate<sup>®</sup> 244 sold by the company Rheox. The products DW 1206F and DW 1206J sold by the company Rohm & Haas may also be used.

[0101] The polyurethane polyethers that may be used herein may also be chosen from those described in the article by G. Fonnum, J. Bakke and Fk. Hansen, in 271 Colloid Polym. Sci 380-389 (1993).

[0102] In one embodiment, a polyurethane polyether that may be obtained by polycondensation of at least three compounds comprising (i) at least one polyethylene glycol comprising from 150 to 180 mol of ethylene oxide, (ii) stearyl alcohol or decyl alcohol, and (iii) at least one diisocyanate may also be used.

[0103] Such polyurethane polyethers are sold, for example, by the company Rohm & Haas under the names Aculyn 46<sup>®</sup> and Aculyn 44<sup>®</sup>. Aculyn 46<sup>®</sup> is a polycondensate of polyethylene glycol comprising 150 or 180 mol of ethylene oxide, of stearyl alcohol and of methylenebis(4-cyclohexyl isocyanate) (SMDI), at 15% by weight in a matrix of maltodextrin (4%) and water (81%); Aculyn 44<sup>®</sup> is a polycondensate of polyethylene glycol comprising 150 or 180 mol of ethylene oxide, of decyl alcohol and of methylenebis(4-cyclohexyl-isocyanate) (SMDI), at 35% by weight in a mixture of propylene glycol (39%) and water (26%).



[0104] Among the polymers derived from associative celluloses that may be used herein, mention may be made, for example, of:

- quaternized cationic celluloses modified with groups comprising at least one hydrophobic chain chosen, for example, from alkyl, arylalkyl and alkylaryl groups comprising at least 8 carbon atoms, or mixtures thereof,
- quaternized cationic hydroxyethylcelluloses modified with groups comprising at least one hydrophobic chain chosen, for example, from alkyl, arylalkyl and alkylaryl groups comprising at least 8 carbon atoms, or mixtures thereof.

[0105] The alkyl radicals borne by the above quaternized celluloses or hydroxyethylcelluloses comprise, for example, from 8 to 30 carbon atoms. The aryl radicals are, for example, chosen from phenyl, benzyl, naphthyl and anthryl groups.

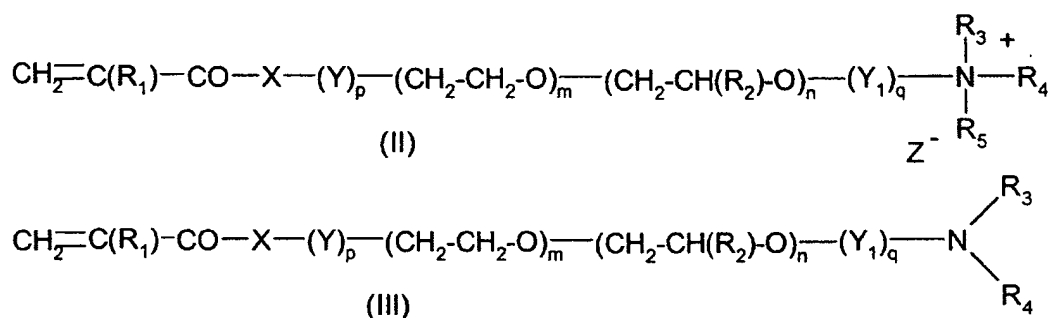
[0106] As examples of quaternized alkylhydroxyethylcelluloses comprising a C<sub>8</sub>-C<sub>30</sub> hydrophobic chain, mention may be made of the products Quatrisoft LM 200®, Quatrisoft LM-X 529-18-A®, Quatrisoft LM-X 529-18B® (C<sub>12</sub> alkyl) and Quatrisoft LM-X 529-8® (C<sub>18</sub> alkyl) sold by the company Amerchol, and the products Crodacel QM®, Crodacel QL® (C<sub>12</sub> alkyl) and Crodacel QS® (C<sub>18</sub> alkyl) sold by the company Croda,

- nonionic cellulose derivatives such as hydroxyethylcelluloses modified with groups comprising at least one hydrophobic chain chosen, for example, from alkyl, arylalkyl and alkylaryl groups, or mixtures thereof, wherein the alkyl groups are chosen, for example, from C<sub>8</sub>-C<sub>22</sub> alkyl groups, for instance the product Natrosol Plus Grade 330 CS® (C<sub>16</sub> alkyl) sold by the company Aqualon, and the product Bermocoll EHM 100® sold by the company Berol Nobel, and
- cellulose derivatives modified with polyalkylene glycol ether alkyl phenol groups, such as the product Amercell Polymer HM-1500® sold by the company Amerchol.

[0107] With regard to the associative polyvinylactams that may be used herein, they may be chosen, for example, from those described in the document FR 0 101 106.

[0108] The polymers are, for example, chosen from cationic polymers and may comprise:

- a) at least one monomer chosen from monomers of vinylactam and alkylvinylactam types;
- b) at least one monomer chosen from monomers of formulae (II) and (III) below:



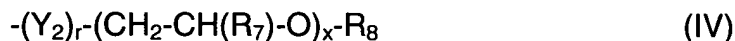
wherein:

[0109] X is chosen from an oxygen atom and a radical NR<sub>6</sub>,

[0110] R<sub>1</sub> and R<sub>6</sub>, which may be identical or different, are each chosen from a hydrogen atom and linear and branched C<sub>1</sub>-C<sub>5</sub> alkyl radicals,

[0111] R<sub>2</sub> is chosen from linear and branched C<sub>1</sub>-C<sub>4</sub> alkyl radicals,

[0112] R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub>, which may be identical or different, are each chosen from a hydrogen atom, linear and branched C<sub>1</sub>-C<sub>30</sub> alkyl radicals and radicals of formula (IV):



[0113] Y, Y<sub>1</sub> and Y<sub>2</sub>, which may be identical or different, are each chosen from linear and branched C<sub>2</sub>-C<sub>16</sub> alkylene radicals,

[0114] R<sub>7</sub> is chosen from a hydrogen atom, linear and branched C<sub>1</sub>-C<sub>4</sub> alkyl radicals, and linear and branched C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl radicals,

[0115]  $R_8$  is chosen from a hydrogen atom and linear and branched  $C_1$ - $C_{30}$  alkyl radicals,

[0116]  $p$ ,  $q$  and  $r$ , which may be identical or different, are each 0 or 1,

[0117]  $m$  and  $n$ , which may be identical or different, are each an integer ranging from 0 to 100,

[0118]  $x$  is an integer ranging from 1 to 100,

[0119]  $Z^-$  is an anion chosen from organic and mineral acid anions,

[0120] with the proviso that:

- at least one of the substituents  $R_3$ ,  $R_4$ ,  $R_5$  and  $R_8$  is chosen from linear and branched  $C_9$ - $C_{30}$  alkyl radicals,
- if  $m$  or  $n$  is other than zero, then  $q$  is equal to 1, and
- if  $m$  or  $n$  is equal to zero, then  $p$  or  $q$  is equal to 0.

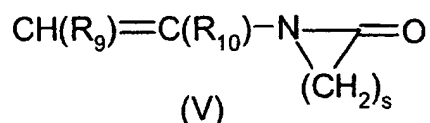
[0121] The poly(vinylactam) polymers disclosed herein may be crosslinked or non-crosslinked and may also be block polymers.

[0122] In one embodiment, the counterion  $Z^-$  of the monomers of the formula (II) is chosen from halide ions, phosphate ions, the methosulphate ion and the tosylate ion.

[0123] In another embodiment,  $R_3$ ,  $R_4$  and  $R_5$ , which may be identical or different, are each chosen from a hydrogen atom and linear and branched  $C_1$ - $C_{30}$  alkyl radicals.

[0124] In yet another embodiment, the monomer b) is a monomer of the formula (II) wherein, for example,  $m$  and  $n$  are equal to zero.

[0125] The vinylactam or alkylvinylactam monomer is, for example, a compound of formula (V):



wherein:

[0126]  $s$  is an integer ranging from 3 to 6,

[0127]  $R_9$  is chosen from a hydrogen atom and  $C_1$ - $C_5$  alkyl radicals,

[0128]  $R_{10}$  is chosen from a hydrogen atom and  $C_1$ - $C_5$  alkyl radicals,

[0129] with the proviso that at least one of the radicals  $R_9$  and  $R_{10}$  is a hydrogen atom.

[0130] In one embodiment, the monomer of the formula (V) is vinylpyrrolidone.

[0131] The poly(vinylactam) polymers disclosed herein may also comprise at least one additional monomer, which is, for example, cationic or nonionic.

[0132] As polymers that may be used herein, mention may be made, for example, of the following terpolymers comprising:

(a) at least one monomer of the formula (V),

(b) at least one monomer of the formula (II) wherein  $p=1$ ,  $q=0$ ,  $R_3$  and  $R_4$ , which may be identical or different, are each chosen from a hydrogen atom and  $C_1$ - $C_5$  alkyl radicals, and  $R_5$  is chosen from  $C_9$ - $C_{24}$  alkyl radicals, and

(c) at least one monomer of the formula (III) wherein  $R_3$  and  $R_4$ , which may be identical or different, are each chosen from a hydrogen atom and  $C_1$ - $C_5$  alkyl radicals.

[0133] In one embodiment, the terpolymers comprising, on a weight basis, from 40% to 95% of the monomer (a), from 0.1% to 55% of the monomer (c) and from 0.25% to 50% of the monomer (b) are used.

[0134] Such polymers are described, for example, in patent application WO 00/68282.

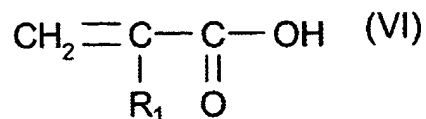
[0135] Poly(vinyl lactam) polymers disclosed herein that may be used include, for example, vinylpyrrolidone/dimethylaminopropylmethacrylamide/dodecyldimethylmethacrylamidopropylammonium tosylate terpolymers, vinylpyrrolidone/dimethylaminopropylmethacrylamide/cocoyldimethylmethacrylamidopropylammonium tosylate terpolymers, vinylpyrrolidone/dimethylaminopropylmethacrylamide/lauryldimethylmethacrylamidopropylammonium tosylate or chloride terpolymers. The vinylpyrrolidone/dimethylaminopropylmethacrylamide/lauryldimethylmethacrylamidopropylammonium chloride terpolymer is sold at a concentration of 20% in water by the company ISP under the name Styleze W20.

[0136] The associative polyvinyl lactam derivatives disclosed herein may also be nonionic copolymers of vinylpyrrolidone and of hydrophobic monomers comprising at least one hydrophobic chain, examples of which that may be mentioned include:

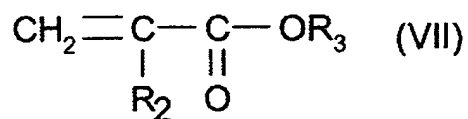
- the products Antaron V216® or Ganex V216® (vinylpyrrolidone/hexadecene copolymer) sold by the company ISP, and
- the products Antaron V220® or Ganex V220® (vinylpyrrolidone/eicosene copolymer) sold by the company ISP.

[0137] Among the associative unsaturated polyacid derivatives that may be mentioned are those comprising at least one hydrophilic unit of olefinic unsaturated carboxylic acid type, and at least one hydrophobic unit of unsaturated carboxylic acid (C<sub>10</sub>-C<sub>30</sub>) alkyl ester type.

[0138] These polymers are chosen, for example, from those in which the hydrophilic unit of olefinic unsaturated carboxylic acid type corresponds to the monomer of formula (VI) below:



wherein R<sub>1</sub> is H, CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>, (*i.e.*, acrylic acid, methacrylic acid or ethacrylic acid units), and wherein the hydrophobic unit of unsaturated carboxylic acid (C<sub>10</sub>-C<sub>30</sub>) alkyl ester type corresponds to the monomer of formula (VII) below:



wherein R<sub>2</sub> is H, CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub> (*i.e.*, acrylate, methacrylate or ethacrylate units); in one embodiment, R<sub>2</sub> is H (acrylate units); in another embodiment, R<sub>2</sub> is CH<sub>3</sub> (methacrylate units); and R<sub>3</sub> is chosen from C<sub>10</sub>-C<sub>30</sub> alkyl radicals, such as C<sub>12</sub>-C<sub>22</sub> alkyl radicals.

[0139] Unsaturated carboxylic acid (C<sub>10</sub>-C<sub>30</sub>) alkyl esters comprise, for example, lauryl acrylate, stearyl acrylate, decyl acrylate, isodecyl acrylate, and dodecyl acrylate, and the corresponding methacrylates, lauryl methacrylate, stearyl methacrylate, decyl methacrylate, isodecyl methacrylate and dodecyl methacrylate.

[0140] Anionic polymers of this type are described and prepared, for example, according to U.S. Patent Nos. 3,915,921 and 4,509,949.

[0141] In anionic associative polymers of this type, polymers that are used are, for example, those formed from a mixture of monomers comprising:

- (i) essentially acrylic acid,
- (ii) an ester of the formula (VII) described above wherein R<sub>2</sub> is H or CH<sub>3</sub>, and R<sub>3</sub> is an alkyl radical chosen from alkyl radicals comprising from 12 to 22 carbon atoms, and

- (iii) a crosslinking agent, which is a well-known copolymerizable polyethylenic unsaturated monomer, for instance diallyl phthalate, allyl (meth)acrylate, divinylbenzene, (poly)ethylene glycol dimethacrylate and methylenebisacrylamide.

[0142] Among the anionic associative polymers of this type are, for example, those comprising from 95% to 60% by weight of acrylic acid (hydrophilic unit), from 4% to 40% by weight of C<sub>10</sub>-C<sub>30</sub> alkyl acrylate (hydrophobic unit) and from 0 to 6% by weight of crosslinking polymerizable monomer, and those comprising from 98% to 96% by weight of acrylic acid (hydrophilic unit), from 1% to 4% by weight of C<sub>10</sub>-C<sub>30</sub> alkyl acrylate (hydrophobic unit) and from 0.1% to 0.6% by weight of crosslinking polymerizable monomer, such as those described above.

[0143] Among the above polymers, the products sold by the company Goodrich under the trade names Pemulen TR1®, Pemulen TR2® and Carbopol 1382®, and the product sold by the company SEPPIC under the name Coatex SX® may, for example, be used. In one embodiment, Pemulen TR1® is used.

[0144] Among the associative unsaturated polyacid derivatives that may also be mentioned are, for example, those comprising among their monomers an  $\alpha,\beta$ -monoethylenically unsaturated carboxylic acid and an ester of an  $\alpha,\beta$ -monoethylenically unsaturated carboxylic acid and of an oxyalkylenated fatty alcohol.

[0145] In one embodiment, these polymers also comprise as monomer at least one ester of an  $\alpha,\beta$ -monoethylenically unsaturated carboxylic acid and of a C<sub>1</sub>-C<sub>4</sub> alcohol.

[0146] Examples of polymers of this type that may be mentioned include Aculyn 22® sold by the company Rohm & Haas, which is a methacrylic acid/ethyl acrylate/stearyl methacrylate oxyalkylenated terpolymer.

[0147] The concentration of the at least one associative polymer in the composition disclosed herein may range, for example, from 0.01% to 10% by weight such as from 0.1% to 5% by weight, relative to the total weight of the composition.

[0148] In the case where the composition is ready-to-use, *i.e.*, when it also comprises at least one oxidizing agent, the concentration of the at least one associative polymer present in the ready-to-use composition may range, for example, from 0.0025% to 10% by weight, such as from 0.025% to 10% by weight, relative to the total weight of the ready-to-use composition.

[0149] The composition disclosed herein also comprises, as an essential constituent component, at least one fluorescent dye.

[0150] As used herein, the term “fluorescent dye” means a dye which is a molecule that colors by itself, and thus absorbs light in the visible spectrum and possibly in the ultraviolet spectrum (wavelengths ranging from 360 to 760 nanometers), but which, in contrast with a standard dye, converts the absorbed energy into fluorescent light of a longer wavelength emitted in the visible region of the spectrum.

[0151] A fluorescent dye as disclosed herein is to be differentiated from an optical brightener. Optical brighteners, which are also known as brighteners, fluorescent brighteners, fluorescent brightening agents, fluorescent whitening agents, whiteners or fluorescent whiteners, are colorless transparent compounds, which do not dye because they do not absorb light in the visible region, but only in the ultraviolet region (wavelengths ranging from 200 to 400 nanometers), and convert the absorbed energy into fluorescent light of a longer wavelength emitted in the visible region of the spectrum; the color impression is then generated solely by purely fluorescent light that is predominantly blue (wavelengths ranging from 400 to 500 nanometers).



[0152] Finally, the fluorescent dye as disclosed herein is soluble in the medium of the composition. It should be pointed out that the fluorescent dye differs therein from a fluorescent pigment, which itself is insoluble in the medium of the composition.

[0153] In one embodiment, the fluorescent dye used herein, which is optionally neutralized, is soluble in the medium of the composition to at least 0.001 g/l, such as at least 0.5 g/l, further such as at least 1 g/l and, even further such as at least 5 g/l at a temperature ranging from 15 to 25°C.

[0154] Moreover, as disclosed herein, the composition does not comprise, as fluorescent dye, a 2-[2-(4-dialkylamino)phenylethenyl]-1-alkylpyridinium wherein the alkyl radical of the pyridinium nucleus is a methyl or ethyl radical, the alkyl radical of the benzene nucleus is a methyl radical, and the counterion is a halide.

[0155] In one embodiment, the composition does not comprise, as fluorescent dye, a compound chosen from azo, azomethine and methine monocationic heterocyclic fluorescent dyes.

[0156] The fluorescent dyes disclosed herein are, for example, dyes in the orange range.

[0157] In one embodiment, the fluorescent dyes disclosed herein lead to a reflectance maximum that is in the wavelength range from 500 to 650 nanometers such as in the wavelength range from 550 to 620 nanometers.

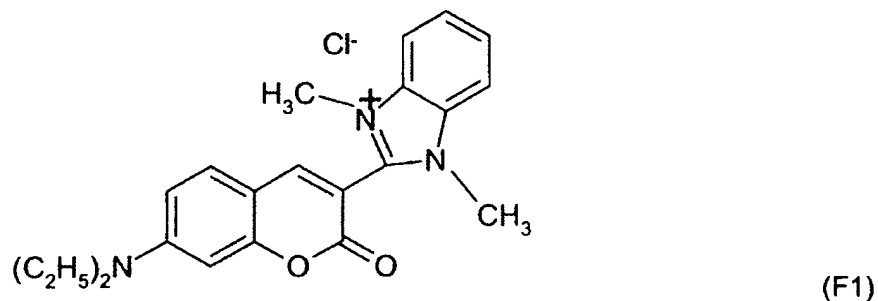
[0158] Some of the fluorescent dyes disclosed herein are compounds that are known per se.

[0159] As examples of fluorescent dyes that may be used, mention may be made, for example, of the fluorescent dyes belonging to the following families: naphthalimides; cationic and non-cationic coumarins; xanthenodiquinolizines (such as sulphorhodamines);

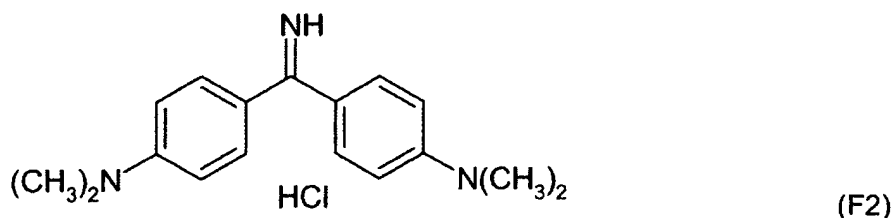
azaxanthenes; naphtholactams; azlactones; oxazines; thiazines; dioxazines; polycationic fluorescent dyes of azo, azomethine and methine types, alone or as mixtures. For example, the fluorescent dyes of the following families can be used: naphthalimides; cationic and non-cationic coumarins; azaxanthenes; naphtholactams; azlactones; oxazines; thiazines; dioxazines; polycationic fluorescent dyes of azo, azomethine and methine types, alone or as mixtures.

[0160] Further, for example, the following may be mentioned among the fluorescent dyes:

- Brilliant Yellow B6GL sold by the company Sandoz and having the following formula (F1):

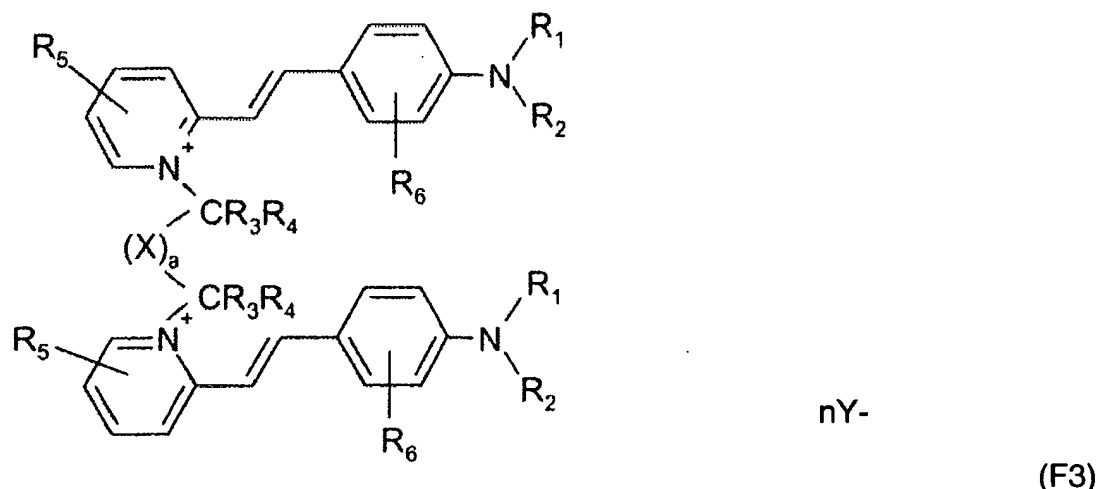


- Basic Yellow 2, or Auramine O, sold by the companies Prolabo, Aldrich or Carlo Erba and having the following formula (F2):



4,4'-(imidocarbonyl)bis(N,N-dimethylaniline) monohydrochloride - CAS number 2465-27-2.

[0161] Mention may also be made of the compounds having the following formula (F3):



wherein:

$R_1$  and  $R_2$ , which may be identical or different, are each chosen from:

- a hydrogen atom;
- linear and branched alkyl radicals comprising from 1 to 10 carbon atoms such as from 1 to 4 carbon atoms, optionally interrupted and/or substituted with at least one entity chosen from hetero atoms and groups comprising at least one hetero atom and/or optionally substituted with at least one halogen atom;
- aryl and arylalkyl radicals, wherein the aryl group comprises 6 carbon atoms and the alkyl radical comprises from 1 to 4 carbon atoms; the aryl radical is optionally substituted with at least one alkyl radical chosen from linear and branched alkyl radicals comprising from 1 to 4 carbon atoms optionally interrupted and/or substituted with at least one entity chosen from hetero atoms and groups comprising at least one hetero atom and/or optionally substituted with at least one halogen atom;
- $R_1$  and  $R_2$  may optionally be linked so as to form a heterocycle with the nitrogen atom and may comprise at least one other hetero atom, wherein the heterocycle is optionally substituted with at least one alkyl radical chosen

from linear and branched alkyl radicals, such as those comprising from 1 to 4 carbon atoms, and is optionally interrupted and/or substituted with at least one entity chosen from hetero atoms and groups comprising at least one hetero atom and/or optionally substituted with at least one halogen atom; and

- R<sub>1</sub> or R<sub>2</sub> may optionally be engaged in a heterocycle comprising the nitrogen atom and one of the carbon atoms of the phenyl group bearing the nitrogen atom;

[0162] R<sub>3</sub> and R<sub>4</sub>, which may be identical or different, are each chosen from a hydrogen atom and alkyl radicals comprising from 1 to 4 carbon atoms;

[0163] R<sub>5</sub>, which may be identical or different, are each chosen from a hydrogen atom, halogen atoms, and linear and branched alkyl radicals comprising from 1 to 4 carbon atoms, optionally interrupted with at least one hetero atom;

[0164] R<sub>6</sub>, which may be identical or different, are each chosen from a hydrogen atom; halogen atoms; and linear and branched alkyl radicals comprising from 1 to 4 carbon atoms, optionally substituted and/or interrupted with at least one entity chosen from hetero atoms and groups bearing at least one hetero atom and/or optionally substituted with at least one halogen atom;

[0165] X is chosen from:

- linear and branched alkyl radicals comprising from 1 to 14 carbon atoms and alkenyl radicals comprising from 2 to 14 carbon atoms, optionally interrupted and/or substituted with at least one entity chosen from hetero atoms and groups comprising at least one hetero atom and/or optionally substituted with at least one halogen atom;
- 5- and 6-membered heterocyclic radicals optionally substituted with at least

one alkyl radical chosen from linear and branched alkyl radicals comprising from 1 to 14 carbon atoms, optionally substituted with at least one hetero atom; optionally substituted with at least one aminoalkyl radical chosen from linear and branched aminoalkyl radicals comprising from 1 to 4 carbon atoms, optionally substituted with at least one hetero atom; and optionally substituted with at least one halogen atom;

- fused and non-fused, aromatic and diaromatic radicals, optionally separated with at least one alkyl radical comprising from 1 to 4 carbon atoms, wherein at least one of the aryl radicals is optionally substituted with at least one halogen atom or with at least one alkyl radical chosen from alkyl radicals comprising from 1 to 10 carbon atoms optionally substituted and/or interrupted with at least one entity chosen from hetero atoms and groups bearing at least one hetero atom; and
- a dicarbonyl radical;
- provided that the group X possibly bears at least one cationic charge;

[0166] a is equal to 0 or 1;

[0167] Y<sup>-</sup>, which may be identical or different, are each an anion chosen from organic and mineral anions; and

[0168] n is an integer at least equal to 2 and at most equal to the number of cationic charges present in the fluorescent compound.

[0169] As used herein, the term "hetero atom" is an oxygen or nitrogen atom.

[0170] Among the groups bearing such hetero atoms that may be mentioned, inter alia, are hydroxyl, alkoxy, carbonyl, amino, ammonium, amido (-N-CO-) and carboxyl (-O-CO- or -CO-O-) groups.

[0171] With regard to the alkenyl groups, they comprise at least one unsaturated carbon-carbon bond ( $\text{-C=C-}$ ). In one embodiment, they comprise only one carbon-carbon double bond.

[0172] In the formula (F3), the radicals  $\text{R}_1$  and  $\text{R}_2$ , which may be identical or different, are chosen, for example, from:

- a hydrogen atom;
- alkyl radicals comprising from 1 to 10 carbon atoms, such as from 1 to 6 carbon atoms, and further such as from 1 to 4 carbon atoms, optionally interrupted with at least one oxygen atom or optionally substituted with at least one entity chosen from hydroxyl, amino and ammonium radicals and chlorine and fluorine atoms;
- benzyl and phenyl radicals optionally substituted with at least one radical chosen from alkyl and alkoxy radicals comprising from 1 to 4 carbon atoms such as from 1 to 2 carbon atoms; and
- with the nitrogen atom, heterocyclic radicals of the pyrrolo, pyrrolidino, imidazolino, imidazolo, imidazolium, pyrazolino, piperazino, morpholino, morpholo, pyrazolo and triazolo types, optionally substituted with at least one alkyl radical chosen from linear and branched alkyl radicals comprising from 1 to 4 carbon atoms optionally interrupted and/or substituted with at least one entity chosen from nitrogen and oxygen atoms and groups bearing at least one atom chosen from nitrogen and oxygen atoms.

[0173] With regard to the abovementioned amino or ammonium radicals, the radicals borne by the nitrogen atom may be identical or different and may, for example, be chosen from a hydrogen atom,  $\text{C}_1\text{-C}_{10}$  alkyl radicals, such as  $\text{C}_1\text{-C}_4$  alkyl radicals and

arylalkyl radicals, wherein, for example, the aryl radical comprises 6 carbon atoms and the alkyl radical comprises from 1 to 10 carbon atoms, such as from 1 to 4 carbon atoms.

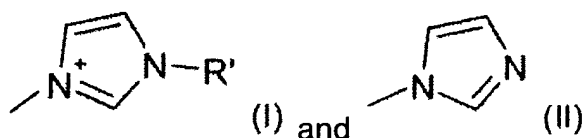
[0174] In one embodiment, the radicals  $R_1$  and  $R_2$ , which may be identical or different, are each chosen from a hydrogen atom; linear and branched  $C_1$ - $C_6$  alkyl radicals;  $C_2$ - $C_6$  alkyl radicals substituted with at least one hydroxyl radical;  $C_2$ - $C_6$  alkyl radicals bearing at least one group chosen from amino and ammonium groups;  $C_2$ - $C_6$  chloroalkyl radicals;  $C_2$ - $C_6$  alkyl radicals interrupted with at least one entity chosen from an oxygen atom and groups bearing at least one oxygen atom (for example, ester); aromatic radicals, for example, phenyl, benzyl and 4-methylphenyl radicals; heterocyclic radicals such as pyrrolo, pyrrolidino, imidazolo, imidazolino, imidazolium, piperazino, morpholo, morpholino, pyrazolo and triazolo radicals, optionally substituted with at least one radical chosen from  $C_1$ - $C_6$  alkyl and aromatic radicals.

[0175] In another embodiment, the radicals  $R_1$  and  $R_2$ , which may be identical or different, are each chosen from a hydrogen atom, linear and branched  $C_1$ - $C_6$  alkyl radicals such as methyl, ethyl, n-butyl and n-propyl radicals; 2-hydroxyethyl radicals; alkyltrimethylammonium and alkyltriethylammonium radicals, wherein the alkyl radical is chosen from linear  $C_2$ - $C_6$  alkyl radicals; (di)alkylmethylamino and (di)alkylethylamino radicals, wherein the alkyl radical is chosen from linear  $C_1$ - $C_6$  alkyl radicals;  $-CH_2CH_2Cl$ ;  $-(CH_2)_n-OCH_3$  and  $-(CH_2)_n-OCH_2CH_3$  wherein n is an integer ranging from 2 to 6;  $-CH_2CH_2-OCOCH_3$ ; and  $-CH_2CH_2COOCH_3$ .

[0176] In yet another embodiment, the radicals  $R_1$  and  $R_2$ , which may be identical or different, (for example, which are identical), are each chosen from a methyl radical and an ethyl radical.

[0177] The radicals  $R_1$  and  $R_2$ , which may be identical or different, may also be chosen from heterocyclic radicals of the pyrrolidino, 3-aminopyrrolidino, 3-(dimethyl)-aminopyrrolidino, 3-(trimethyl)aminopyrrolidino, 2,5-dimethylpyrrolo, 1H-imidazolo, 4-methylpiperazino, 4-benzylpiperazino, morpholo, 3,5-(tert-butyl)-1H-pyrazolo, 1H-pyrazolo and 1H-1,2,4-triazolo types.

[0178] The radicals  $R_1$  and  $R_2$ , which may be identical or different, may also be chosen and be linked so as to form a heterocycle chosen from heterocycles of formulae (I) and (II) below:



wherein  $R'$  is chosen from a hydrogen atom,  $C_1$ - $C_3$  alkyl radicals,  $-CH_2CH_2OH$ , and  $-CH_2CH_2OCH_3$ .

[0179] In one embodiment,  $R_5$ , which may be identical or different, are each chosen from a hydrogen atom, fluorine and chlorine atoms, and linear and branched alkyl radicals comprising from 1 to 4 carbon atoms optionally interrupted with at least one atom chosen from oxygen and nitrogen atoms.

[0180] The substituent  $R_5$ , if it is other than hydrogen, is, for example, in at least one position chosen from positions 3 and 5 relative to the carbon of the ring bearing the nitrogen substituted with the radicals  $R_1$  and  $R_2$ . In one embodiment, the substituent  $R_5$  is in position 3 relative to that carbon.

[0181] For example, the radicals  $R_5$ , which may be identical or different, are each chosen from a hydrogen atom; linear and branched  $C_1$ - $C_4$  alkyl radicals;  $-O-R_{51}$  radicals wherein  $R_{51}$  is chosen from linear  $C_1$ - $C_4$  alkyl radicals;  $-R_{52}-O-CH_3$  radicals wherein  $R_{52}$  is chosen from linear  $C_2$ - $C_3$  alkyl radicals;  $-R_{53}-N(R_{54})_2$  radicals wherein  $R_{53}$  is chosen from



linear C<sub>2</sub>-C<sub>3</sub> alkyl radicals and R<sub>54</sub>, which may be identical or different, are chosen from a hydrogen atom and a methyl radical.

[0182] Further, for example, R<sub>5</sub>, which may be identical or different, is chosen from hydrogen, methyl and methoxy radicals. In one embodiment, R<sub>5</sub> is a hydrogen atom.

[0183] In another embodiment, the radicals R<sub>6</sub>, which may be identical or different, are each chosen from a hydrogen atom; linear and branched C<sub>1</sub>-C<sub>4</sub> alkyl radicals; -X' radicals, wherein X' is chosen from chlorine, bromine and fluorine atoms; -R<sub>61</sub>-O-R<sub>62</sub> radicals wherein R<sub>61</sub> is chosen from linear C<sub>2</sub>-C<sub>3</sub> alkyl radicals and R<sub>62</sub> is a methyl radical; -R<sub>63</sub>-N(R<sub>64</sub>)<sub>2</sub> radicals wherein R<sub>63</sub> is chosen from linear C<sub>2</sub>-C<sub>3</sub> alkyl radicals and R<sub>64</sub>, which may be identical or different, are each chosen from a hydrogen atom and a methyl radical; -N(R<sub>65</sub>)<sub>2</sub> radicals wherein R<sub>65</sub>, which may be identical or different, are each chosen from a hydrogen atom and linear C<sub>2</sub>-C<sub>3</sub> alkyl radicals; -NHCO R<sub>66</sub> radicals wherein R<sub>66</sub> is chosen from C<sub>1</sub>-C<sub>2</sub> alkyl radicals, C<sub>1</sub>-C<sub>2</sub> chloroalkyl radicals, radicals -R<sub>67</sub>-NH<sub>2</sub>, -R<sub>67</sub>-NH(CH<sub>3</sub>), -R<sub>67</sub>-N(CH<sub>3</sub>)<sub>2</sub>, -R<sub>67</sub>-N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>, and -R<sub>67</sub>-N<sup>+</sup>(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> wherein R<sub>67</sub> is chosen from C<sub>1</sub>-C<sub>2</sub> alkyl radicals.

[0184] The substituent R<sub>6</sub>, if it is other than hydrogen, is, for example, in at least one position chosen from positions 2 and 4 relative to the nitrogen atom of the pyridinium ring. In one embodiment, the substituent R<sub>6</sub> is in position 4 relative to that nitrogen atom.

[0185] For example, these radicals R<sub>6</sub>, which may be identical or different, are each chosen from a hydrogen atom and methyl and ethyl radicals. In one embodiment, R<sub>6</sub> is a hydrogen atom.

[0186] Radicals R<sub>3</sub> and R<sub>4</sub>, which may be identical or different, are each, for example, chosen from a hydrogen atom and alkyl radicals comprising from 1 to 4 carbon

atoms. In one embodiment, radicals  $R_3$  and  $R_4$  are each a methyl radical. In another embodiment, radicals  $R_3$  and  $R_4$  are each a hydrogen atom.

[0187] As mentioned above, X is chosen, for example, from:

- linear and branched alkyl radicals comprising from 1 to 14 carbon atoms and alkenyl radicals comprising from 2 to 14 carbon atoms, optionally interrupted and/or substituted with at least one entity chosen from hetero atoms, and groups bearing at least one hetero atom, and optionally substituted with at least one halogen atom;
- 5- and 6-membered heterocyclic radicals optionally substituted with at least one alkyl radical chosen from linear and branched alkyl radicals comprising from 1 to 14 carbon atoms; optionally substituted with at least one aminoalkyl radical chosen from linear and branched aminoalkyl radicals comprising from 1 to 4 carbon atoms, optionally substituted with at least one hetero atom; and optionally substituted with at least one halogen atom;
- fused and non-fused, aromatic and diaromatic radicals, optionally separated with at least one alkyl radical chosen from alkyl radicals comprising from 1 to 4 carbon atoms, wherein at least one of the aryl radicals is optionally substituted with at least one halogen atom or with at least one alkyl radical chosen from alkyl radicals comprising from 1 to 10 carbon atoms optionally substituted and/or interrupted with at least one entity chosen from hetero atoms and groups bearing at least one hetero atom; and
- a dicarbonyl radical.

[0188] In addition, the group X may bear at least one cationic charge.

[0189] Thus, X may be chosen, for example, from linear and branched alkyl radicals comprising from 1 to 14 carbon atoms and alkenyl radicals comprising from 2 to 14 carbon atoms, may be substituted and/or interrupted with at least one entity chosen from oxygen and nitrogen atoms and groups bearing at least one hetero atom, and may be substituted with at least one atom chosen from fluorine and chlorine atoms. Among the groups of this type that may be mentioned, for example, are hydroxyl, alkoxy (such as with a radical R of the C<sub>1</sub>-C<sub>4</sub> alkyl type), amino, ammonium, amido, carbonyl and carboxyl groups (-COO- or -O-CO-) such as with a radical of alkyloxy type.

[0190] The nitrogen atom, if present, may be in a quaternized or non-quaternized form. In this case, the other radical or the other two radicals borne by the quaternized or non-quaternized nitrogen atom can be identical or different and may be chosen from a hydrogen atom and C<sub>1</sub>-C<sub>4</sub> alkyl radicals, such as a methyl radical.

[0191] In one embodiment, the group X is chosen from 5- and 6-membered heterocyclic radicals of the imidazolo, pyrazolo, triazino and pyridino types, optionally substituted with at least one alkyl radical chosen from linear and branched alkyl radicals comprising from 1 to 14 carbon atoms, such as from 1 to 10 carbon atoms, and further such as from 1 to 4 carbon atoms; optionally substituted with at least one aminoalkyl radical chosen from linear and branched aminoalkyl radicals comprising from 1 to 10 carbon atoms, and such as from 1 to 4 carbon atoms, optionally substituted with at least one group comprising at least one hetero atom (such as a hydroxyl radical); and optionally substituted with at least one halogen atom. For example, the amino group can be linked to the heterocycle.

[0192] In another embodiment, the group X is chosen from aromatic radicals comprising, for example, 6 carbon atoms, fused and non-fused diaromatic radicals

comprising, for example, from 10 to 12 carbon atoms, possibly separated with at least one alkyl radical chosen from alkyl radicals comprising from 1 to 4 carbon atoms, wherein at least one of the aryl radicals is optionally substituted with at least one entity chosen from halogen atoms and alkyl radicals comprising from 1 to 10 carbon atoms, such as from 1 to 4 carbon atoms, optionally interrupted with at least one entity chosen from oxygen and nitrogen atoms and groups comprising at least one hetero atom, for example, carbonyl, carboxyl, amido, amino and ammonium radicals.

[0193] The aromatic radical, such as a phenyl radical, is linked to the groups  $CR_3R_4$  via bonds in positions 1,2, 1,3 or 1,4 such as in positions 1,3 and 1,4. If the phenyl radical linked via bonds in positions 1,4 bears one or two substituents, this or these substituent(s) is(are), for example, located in position 1,4 relative to one of the groups  $CR_3R_4$ . If the phenyl radical linked via bonds in positions 1,3 bears one or two substituents, this or these substituent(s) is (are), for example, located in position 1 and/or 3 relative to one of the groups  $CR_3R_4$ .

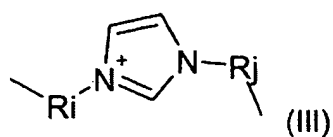
[0194] In the case where the radical is diaromatic, it is, for example, non-fused and comprises two phenyl radicals possibly separated with a single bond (*i.e.*, a carbon of each of the two rings) or with an alkyl radical, such as of  $CH_2$  or  $C(CH_3)_2$  type. In one embodiment, the aromatic radicals do not bear a substituent. It should be noted that the diaromatic radical is linked to the groups  $CR_3R_4$  via bonds in positions 4,4'.

[0195] The groups X that are suitable may be chosen, for example, from linear and branched alkyl radicals comprising from 1 to 13 carbon atoms, such as methylene, ethylene, propylene, isopropylene, n-butylene, pentylene and hexylene; 2-hydroxypropylene and 2-hydroxy-n-butylene;  $C_1$ - $C_{13}$  alkylene radicals substituted or interrupted with at least one entity chosen from nitrogen and oxygen atoms, and groups

bearing at least one hetero atom (for example, hydroxyl, amino, ammonium, carbonyl and carboxyl), such as  $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$ , 1,6-dideoxy-d-mannitol,  $-\text{CH}_2\text{N}^+(\text{CH}_3)_2\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_2-(\text{CH}_2)_6\text{N}^+(\text{CH}_3)_2-\text{CH}_2\text{CH}_2-$ ,  $-\text{CO}-\text{CO}-$ , 3,3-dimethylpentylene, 2-acetoxyethylene, butylene-1,2,3,4-tetraol;  $-\text{CH}=\text{CH}-$ ; aromatic and diaromatic radicals substituted with at least one entity chosen from alkyl radicals, groups bearing at least one hetero atom and halogen atoms, such as 1,4-phenylene, 1,3-phenylene, 1,2-phenylene, 2,6-fluorobenzene, 4,4'-biphenylene, 1,3-(5-methylbenzene), 1,2-bis(2-methoxy)benzene, bis(4-phenyl)methane, methyl 3,4-benzoate and 1,4-bis(amidomethyl)phenyl; radicals of heterocyclic type such as pyridine, and derivatives thereof such as 2,6-bispyridine, imidazole, imidazolium and triazine.

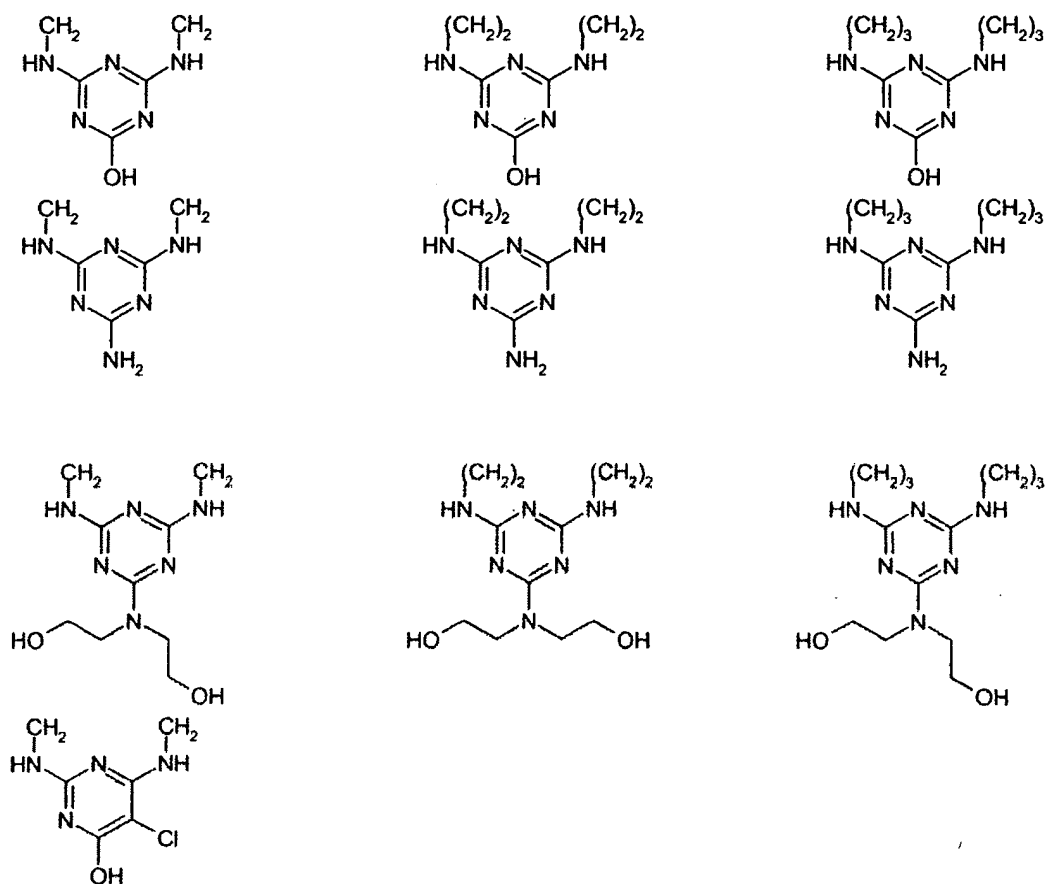
[0196] In one embodiment, X is chosen from linear and branched  $\text{C}_1$ - $\text{C}_{13}$  alkyl radicals;  $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-$ ;  $-\text{CH}_2\text{CH}(\text{Cl})\text{CH}_2-$ ;  $-\text{CH}_2\text{CH}_2-\text{OCOCH}_2-$ ;  $-\text{CH}_2\text{CH}_2\text{COOCH}_2-$ ;  $-\text{Ra}-\text{O}-\text{Rb}-$  radicals wherein Ra is chosen from linear  $\text{C}_2$ - $\text{C}_6$  alkyl radicals and Rb is chosen from  $\text{C}_1$ - $\text{C}_2$  alkyl radicals;  $-\text{Rc}-\text{N}(\text{Rd})-\text{Re}-$  radicals wherein Rc is chosen from  $\text{C}_2$ - $\text{C}_9$  alkyl radicals, Rd is chosen from a hydrogen atom and  $\text{C}_1$ - $\text{C}_2$  alkyl radicals and Re is chosen from  $\text{C}_1$ - $\text{C}_6$  alkyl radicals;  $-\text{Rf}-\text{N}^+(\text{Rg})_2-\text{Rh}-$  radicals wherein Rf is chosen from linear  $\text{C}_2$ - $\text{C}_9$  alkyl radicals, Rg, which may be identical or different, (for example, which are identical), are each chosen from  $\text{C}_1$ - $\text{C}_2$  alkyl radicals and Rh is chosen from linear  $\text{C}_1$ - $\text{C}_6$  alkyl radicals; and  $-\text{CO}-\text{CO}-$ .

[0197] X may furthermore be chosen, for example, from imidazole radicals, optionally substituted with at least one alkyl radical chosen from alkyl radicals comprising from 1 to 14 carbon atoms, such as from 1 to 10 carbon atoms and further such as from 1 to 4 carbon atoms, for example, the divalent radicals having the following formula (III):

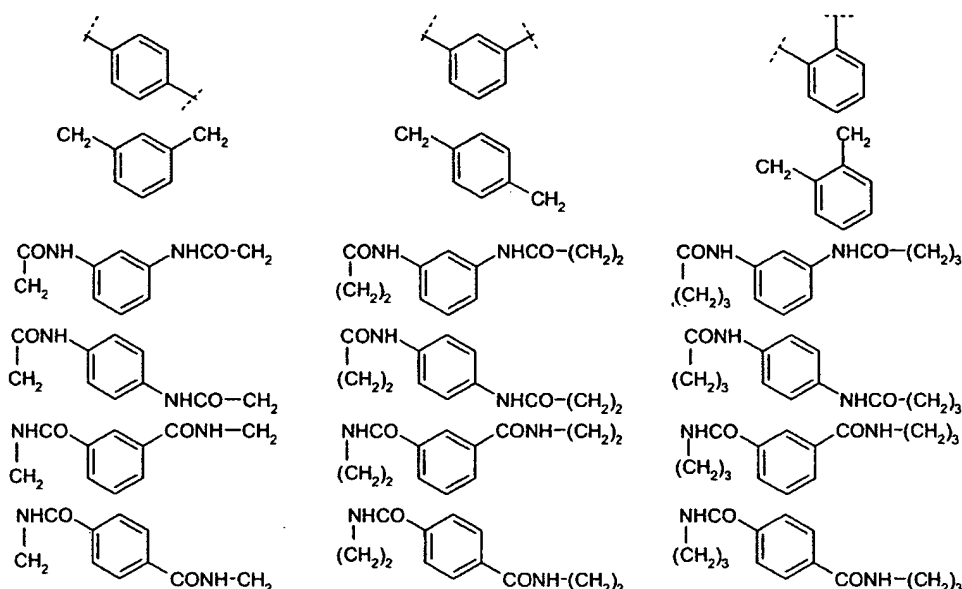


wherein Ri and Rj, which may be identical or different, are each chosen from linear C<sub>1</sub>-C<sub>6</sub> alkyl radicals;

[0198] X may similarly be chosen, for example, from the divalent triazine-based radicals below:



[0199] In one embodiment, X may be chosen from the divalent aromatic radicals below:



[0200] In the formula (F3) of these fluorescent compounds,  $\text{Y}^-$  is an anion chosen from organic and mineral anions. If there are several anions  $\text{Y}^-$ , these anions may be identical or different.

[0201] Among the anions of mineral origin that may be mentioned, examples include anions derived from halogen atoms, such as chlorides and iodides, sulphates and bisulphates, nitrates, phosphates, hydrogen phosphates, dihydrogen phosphates, carbonates and bicarbonates.

[0202] Among the anions of organic origin that may be mentioned, examples include anions derived from the salts of saturated or unsaturated, aromatic or non-aromatic monocarboxylic or polycarboxylic, sulphonic or sulphuric acids, optionally substituted with at least one entity chosen from hydroxyl and amino radicals, and halogen atoms. Non-limiting examples that are suitable for use include acetates, hydroxyacetates, aminoacetates, (tri)chloroacetates, benzoxyacetates, propionates and derivatives bearing at least one chlorine atom, fumarates, oxalates, acrylates, malonates, succinates, lactates,

tartrates, glycolates, citrates, benzoates and derivatives bearing at least one radical chosen from methyl and amino radicals, alkyl sulphates, tosylates, benzenesulphonates, toluene-sulphonates, etc.

[0203] In one embodiment,  $Y^-$ , which may be identical or different, are each chosen from chloride, sulphate, methosulphate and ethosulphate.

[0204] Finally, the integer  $n$  is at least equal to 2 and at most equal to the number of cationic charges present in the fluorescent compound.

[0205] For example, the fluorescent compounds that have just been described in detail are symmetrical compounds.

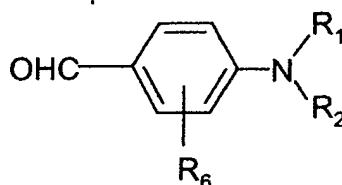
[0206] These compounds may be synthesized by reacting, in a first step,  $\alpha$ -picoline with a reagent comprising two leaving groups that may be chosen from halogen atoms, such as bromine and chlorine, or groups of tolylsulphonyl or methanesulphonyl type.

[0207] This first step may take place in the presence of a solvent, for instance dimethylformamide.

[0208] The number of moles of  $\alpha$ -picoline is generally in the range of 2 per mole of reagent comprising the leaving groups.

[0209] In addition, the reaction is usually performed at the reflux temperature of the reagent and/or of the solvent if a solvent is present.

[0210] The product derived from this first step is then placed in contact with a corresponding aldehyde having the following formula:



wherein  $R_1$ ,  $R_2$  and  $R_6$  have the same meanings as indicated above in the formula (F3).



[0211] In this case, the reaction may be performed in the presence of a suitable solvent, which is, for example, at reflux.

[0212] The radicals  $R_1$  and  $R_2$  of the aldehyde may have the meaning indicated in the formula (F3) described previously.

[0213] It is also possible to use an aldehyde wherein the radicals  $R_1$ ,  $R_2$  and  $R_6$  are hydrogen atoms and to perform, in accordance with standard methods, the substitution of these hydrogen atoms with suitable radicals as described in the general formula once the second step is complete.

[0214] Reference may be made, for example, to syntheses as described in U.S. Patent No. 4,256,458.

[0215] The at least one fluorescent dye present in the composition disclosed herein may range, for example, from 0.01% to 20% by weight, such as from 0.05% to 10% by weight, and further such as from 0.1% to 5% by weight, relative to the total weight of the composition.

[0216] The cosmetically acceptable medium generally comprises water or a mixture of water and at least one organic solvent chosen from common organic solvents.

[0217] Among the solvents that are suitable for use, mention may be made, for example, of alcohols such as ethyl alcohol, isopropyl alcohol, benzyl alcohol and phenylethyl alcohol, glycols and glycol ethers, for instance ethylene glycol monomethyl ether, monoethyl ether and monobutyl ether, propylene glycol and ethers thereof, for instance propylene glycol monomethyl ether, butylene glycol, dipropylene glycol and diethylene glycol alkyl ethers, for instance diethylene glycol monoethyl ether and monobutyl ether, and polyols, for instance glycerol. Polyethylene glycols and polypropylene glycols, and mixtures of all these compounds, may also be used.

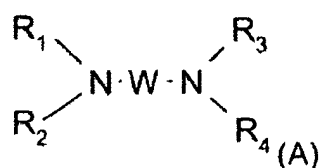
[0218] The at least one solvent, if present, is in an amount ranging, for example, from 1% to 40% by weight such as from 5% to 30% by weight relative to the total weight of the composition.

[0219] The pH of the composition disclosed herein ranges, for example, from 3 to 12, such as from 5 to 11.

[0220] It may be adjusted to the desired value by means of acidifying or basifying agents.

[0221] Examples of acidifying agents that may be mentioned include mineral or organic acids, for instance hydrochloric acid, orthophosphoric acid, sulphuric acid, carboxylic acids, for instance acetic acid, tartaric acid, citric acid and lactic acid, and sulphonic acids.

[0222] Examples of basifying agents that may be mentioned include aqueous ammonia, alkaline carbonates, alkanolamines such as monoethanolamine, diethanolamine and triethanolamine and derivatives thereof, sodium hydroxide, potassium hydroxide and the compounds of formula (A) below:



wherein W is a propylene residue optionally substituted with at least one entity chosen from a hydroxyl group and C<sub>1</sub>-C<sub>6</sub> alkyl radicals; R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub>, which may be identical or different, are each chosen from a hydrogen atom and C<sub>1</sub>-C<sub>6</sub> alkyl and C<sub>1</sub>-C<sub>6</sub> hydroxyalkyl radicals.

[0223] In one embodiment, the composition may comprise, in addition to the at least one fluorescent dye, at least one additional non-fluorescent direct dye chosen from

those of nonionic, cationic or anionic nature, which may be chosen, for example, from nitrobenzene dyes.

[0224] The following red or orange nitrobenzene direct dyes are, for example, suitable for use:

- 1-hydroxy-3-nitro-4-N-( $\gamma$ -hydroxypropyl)aminobenzene,
- N-( $\beta$ -hydroxyethyl)amino-3-nitro-4-aminobenzene,
- 1-amino-3-methyl-4-N-( $\beta$ -hydroxyethyl)amino-6-nitrobenzene,
- 1-hydroxy-3-nitro-4-N-( $\beta$ -hydroxyethyl)aminobenzene,
- 1,4-diamino-2-nitrobenzene,
- 1-amino-2-nitro-4-methylaminobenzene,
- N-( $\beta$ -hydroxyethyl)-2-nitro-para-phenylenediamine,
- 1-amino-2-nitro-4-( $\beta$ -hydroxyethyl)amino-5-chlorobenzene,
- 2-nitro-4-aminodiphenylamine,
- 1-amino-3-nitro-6-hydroxybenzene,
- 1-( $\beta$ -aminoethyl)amino-2-nitro-4-( $\beta$ -hydroxyethoxy)benzene,
- 1-( $\beta,\gamma$ -dihydroxypropyl)oxy-3-nitro-4-( $\beta$ -hydroxyethyl)aminobenzene,
- 1-hydroxy-3-nitro-4-aminobenzene,
- 1-hydroxy-2-amino-4,6-dinitrobenzene,
- 1-methoxy-3-nitro-4-( $\beta$ -hydroxyethyl)aminobenzene,
- 2-nitro-4'-hydroxydiphenylamine, and
- 1-amino-2-nitro-4-hydroxy-5-methylbenzene.

[0225] The composition disclosed herein may also comprise, in addition to or in replacement for these nitrobenzene dyes, at least one additional direct dye chosen from

yellow, green-yellow, blue and violet nitrobenzene dyes, azo dyes, anthraquinone, naphthoquinone and benzoquinone dyes, indigoid dyes, and triarylmethane-based dyes.

[0226] The at least one additional direct dye may, for example, be chosen from basic dyes, among which mention may be made, for example, of the dyes known in the Color Index, 3rd edition, under the names "Basic Brown 16", "Basic Brown 17", "Basic Yellow 57", "Basic Red 76", "Basic Violet 10", "Basic Blue 26" and "Basic Blue 99", and acidic direct dyes, among which mention may be made, for example, of the dyes known in the Color Index, 3rd edition, under the names "Acid Orange 7", "Acid Orange 24", "Acid Yellow 36", "Acid Red 33", "Acid Red 184", "Acid Black 2", "Acid Violet 43" and "Acid Blue 62", and cationic direct dyes such as those described in patent applications WO 95/01772, WO 95/15144 and EP-A-0 714 954.

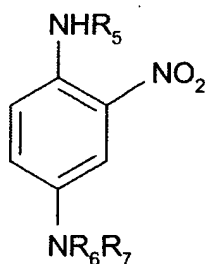
[0227] Among the additional yellow and green-yellow nitrobenzene direct dyes that may be mentioned, for example, are the compounds chosen from:

- 1- $\beta$ -hydroxyethoxy-3-methylamino-4-nitrobenzene,
- 1-methylamino-2-nitro-5-( $\beta,\gamma$ -dihydroxypropyl)oxybenzene,
- 1-( $\beta$ -hydroxyethyl)amino-2-methoxy-4-nitrobenzene,
- 1-( $\beta$ -aminoethyl)amino-2-nitro-5-methoxybenzene,
- 1,3-di( $\beta$ -hydroxyethyl)amino-4-nitro-6-chlorobenzene,
- 1-amino-2-nitro-6-methylbenzene,
- 1-( $\beta$ -hydroxyethyl)amino-2-hydroxy-4-nitrobenzene,
- N-( $\beta$ -hydroxyethyl)-2-nitro-4-trifluoromethylaniline,
- 4-( $\beta$ -hydroxyethyl)amino-3-nitrobenzenesulphonic acid,
- 4-ethylamino-3-nitrobenzoic acid,
- 4-( $\beta$ -hydroxyethyl)amino-3-nitrochlorobenzene,

- 4-( $\beta$ -hydroxyethyl)amino-3-nitromethylbenzene,
- 4-( $\beta,\gamma$ -dihydroxypropyl)amino-3-nitrotrifluoromethylbenzene,
- 1-( $\beta$ -ureidoethyl)amino-4-nitrobenzene,
- 1,3-diamino-4-nitrobenzene,
- 1-hydroxy-2-amino-5-nitrobenzene,
- 1-amino-2-[tris(hydroxymethyl)methyl]amino-5-nitrobenzene,
- 1-( $\beta$ -hydroxyethyl)amino-2-nitrobenzene, and
- 4-( $\beta$ -hydroxyethyl)amino-3-nitrobenzamide.

[0228] Among the additional blue or violet nitrobenzene direct dyes that may be mentioned, for example, are the compounds chosen from:

- 1-( $\beta$ -hydroxyethyl)amino-4-N,N-bis( $\beta$ -hydroxyethyl)amino-2-nitrobenzene,
- 1-( $\gamma$ -hydroxypropyl)amino-4,N,N-bis( $\beta$ -hydroxyethyl)amino-2-nitrobenzene,
- 1-( $\beta$ -hydroxyethyl)amino-4-(N-methyl-N- $\beta$ -hydroxyethyl)amino-2-nitrobenzene,
- 1-( $\beta$ -hydroxyethyl)amino-4-(N-ethyl-N- $\beta$ -hydroxyethyl)amino-2-nitrobenzene,
- 1-( $\beta,\gamma$ -dihydroxypropyl)amino-4-(N-ethyl-N- $\beta$ -hydroxyethyl)amino-2-nitrobenzene,
- 2-nitroparaphenylenediamines having the following formula:



wherein:

- $R_6$  is chosen from  $C_1$ - $C_4$  alkyl radicals, and  $\beta$ -hydroxyethyl,  $\beta$ -hydroxypropyl and  $\gamma$ -hydroxypropyl radicals;

- R<sub>5</sub> and R<sub>7</sub>, which may be identical or different, are each chosen from  $\beta$ -hydroxyethyl,  $\beta$ -hydroxypropyl,  $\gamma$ -hydroxypropyl and  $\beta,\gamma$ -dihydroxypropyl radicals, provided that at least one of the radical chosen from radicals R<sub>5</sub>, R<sub>6</sub> and R<sub>7</sub> is a  $\gamma$ -hydroxypropyl radical and R<sub>6</sub> and R<sub>7</sub> are not simultaneously able to denote a  $\beta$ -hydroxyethyl radical when R<sub>6</sub> is a  $\gamma$ -hydroxypropyl radical, such as those described in the document FR 2 692 572.

[0229] When present, the at least one additional direct dye is present in an amount ranging, for example, from 0.0005% to 12% by weight, such as from 0.005% to 6% by weight relative to the total weight of the composition.

[0230] When it is intended for oxidation dyeing, the composition disclosed herein comprises, in addition to the at least one fluorescent dye, at least one oxidation base chosen from the oxidation bases conventionally used for oxidation dyeing and among which mention may be made, for example, of para-phenylenediamines, bis(phenyl)alkylenediamines, para-aminophenols, ortho-aminophenols and heterocyclic bases, and the acid or base addition salts thereof.

[0231] Among the para-phenylenediamines that may be mentioned, for example, are para-phenylenediamine, para-tolylenediamine, 2-chloro-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,5-dimethyl-para-phenylenediamine, N,N-dimethyl-para-phenylenediamine, N,N-diethyl-para-phenylenediamine, N,N-dipropyl-para-phenylenediamine, 4-amino-N,N-diethyl-3-methylaniline, N,N-bis( $\beta$ -hydroxyethyl)-para-phenylenediamine, 4-N,N-bis( $\beta$ -hydroxyethyl)amino-2-methylaniline, 4-N,N-bis( $\beta$ -hydroxyethyl)amino-2-chloroaniline, 2- $\beta$ -hydroxyethyl-para-phenylenediamine, 2-fluoro-para-phenylenediamine, 2-isopropyl-para-phenylenediamine, N-( $\beta$ -hydroxypropyl)-para-

phenylenediamine, 2-hydroxymethyl-para-phenylenediamine, N,N-dimethyl-3-methyl-para-phenylenediamine, N-ethyl-N-( $\beta$ -hydroxyethyl)-para-phenylenediamine, N-( $\beta,\gamma$ -dihydroxypropyl)-para-phenylenediamine, N-(4'-aminophenyl)-para-phenylenediamine, N-phenyl-para-phenylenediamine, 2- $\beta$ -hydroxyethyloxy-para-phenylenediamine, 2- $\beta$ -acetaminoethyloxy-para-phenylenediamine, N-( $\beta$ -methoxyethyl)-para-phenylenediamine and 4'-aminophenyl-1-(3-hydroxy)pyrrolidine, and the acid or base addition salts thereof.

[0232] Among the para-phenylenediamines mentioned above, examples include para-phenylenediamine, para-tolylenediamine, 2-isopropyl-para-phenylenediamine, 2- $\beta$ -hydroxyethyl-para-phenylenediamine, 2- $\beta$ -hydroxyethyloxy-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, N,N-bis( $\beta$ -hydroxyethyl)-para-phenylenediamine, 2-chloro-para-phenylenediamine and 2- $\beta$ -acetaminoethyloxy-para-phenylenediamine, and the acid or base addition salts thereof.

[0233] Among the bis(phenyl)alkylenediamines that may be mentioned, for example, are N,N'-bis( $\beta$ -hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol, N,N'-bis( $\beta$ -hydroxyethyl)-N,N'-bis(4'-aminophenyl)ethylenediamine, N,N'-bis(4'-aminophenyl)tetramethylenediamine, N,N'-bis( $\beta$ -hydroxyethyl)-N,N'-bis(4'-aminophenyl)tetramethylenediamine, N,N'-bis(4'-methylaminophenyl)tetramethylenediamine, N,N'-bis(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)ethylenediamine and 1,8-bis(2,5-diaminophenoxy)-3,5-dioxaoctane, and the acid or base addition salts thereof.

[0234] Among the para-aminophenols that may be mentioned, for example, are para-aminophenol, 4-amino-3-methylphenol, 4-amino-3-fluorophenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-hydroxymethylphenol,

4-amino-2-methoxymethylphenol, 4-amino-2-aminomethylphenol, 4-amino-2-( $\beta$ -hydroxyethylaminomethyl)phenol and 4-amino-2-fluorophenol, and the acid or base addition salts thereof.

[0235] Among the ortho-aminophenols that may be mentioned, for example, are 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol and 5-acetamido-2-aminophenol, and the acid or base addition salts thereof.

[0236] Among the heterocyclic bases that may be mentioned, for example, are pyridine derivatives, pyrimidine derivatives and pyrazole derivatives, and the acid or base addition salts thereof.

[0237] When present, the at least one oxidation base is present in an amount ranging, for example, from 0.0005% to 12% by weight, such as from 0.005% to 6% by weight relative to the total weight of the composition.

[0238] When it is intended for oxidation dyeing, the composition disclosed herein may also comprise, in addition to the at least one fluorescent dye and the at least one oxidation base, at least one coupler so as to modify or to enrich with glints the shades obtained using the at least one fluorescent dye and the at least one oxidation base.

[0239] The at least one coupler that may be used in the composition disclosed herein may be chosen from the couplers conventionally used in oxidation dyeing, and among which mention may be made, for example, of meta-phenylenediamines, meta-aminophenols, meta-diphenols and heterocyclic couplers, and the acid or base addition salts thereof.

[0240] The at least one coupler disclosed herein may be, for example, chosen from 2-methyl-5-aminophenol, 5-N-( $\beta$ -hydroxyethyl)amino-2-methylphenol, 3-aminophenol, 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro-1,3-dihydroxybenzene,



2,4-diamino-1-( $\beta$ -hydroxyethyloxy)benzene, 2-amino-4-( $\beta$ -hydroxyethylamino)-1-methoxybenzene, 1,3-diaminobenzene, 1,3-bis(2,4-diaminophenoxy)propane, sesamol,  $\alpha$ -naphthol, 6-hydroxyindole, 4-hydroxyindole, 4-hydroxy-N-methylindole, 6-hydroxyindoline, 2,6-dihydroxy-4-methylpyridine, 1H-3-methylpyrazol-5-one, 1-phenyl-3-methylpyrazol-5-one, 2,6-dimethylpyrazolo[1,5-b]-1,2,4-triazole, 2,6-dimethyl[3,2-c]-1,2,4-triazole and 6-methylpyrazolo[1,5-a]benzimidazole, and the acid and base addition salts thereof.

[0241] When present, the at least one coupler is present in an amount ranging from 0.0001% to 10% by weight such as from 0.005% to 5% by weight, relative to the total weight of the composition.

[0242] In general, the acid addition salts that may be used in the context of the compositions disclosed herein (oxidation bases and couplers) are chosen, for example, from hydrochlorides, hydrobromides, sulphates, citrates, succinates, tartrates, tosylates, benzenesulphonates, lactates and acetates.

[0243] The base addition salts that may be used in the context of the compositions disclosed herein (oxidation bases and couplers) are chosen, for example, from the addition salts with alkali metals, alkaline-earth metals, ammonia and organic amines, including alkanolamines and the compounds of formula (VIII).

[0244] The composition disclosed herein may also comprise at least one adjuvant chosen from various conventionally used adjuvants, such as anionic, cationic, nonionic, amphoteric and zwitterionic surfactants and mixtures thereof, anionic, cationic, nonionic, amphoteric and zwitterionic polymers other than those disclosed herein, and mixtures thereof, mineral thickeners, antioxidants, penetrating agents, sequestering agents, fragrances, buffers, dispersants, conditioners, for instance cations, volatile and non-volatile,

modified and unmodified silicones, film-forming agents, ceramides, preserving agents, stabilizers and opacifiers.

[0245] Non-associative organic thickening polymers may also be added.

[0246] When at least one surfactant is present, such as of nonionic, anionic or amphoteric type, it is present in an amount ranging, for example, from 0.01% to 30% by weight relative to the weight of the composition.

[0247] Needless to say, a person skilled in the art will take care to select this or these optional additional compound(s) such that the advantageous properties intrinsically associated with the composition disclosed herein are not, or are not substantially, adversely affected by the envisaged addition(s).

[0248] The composition disclosed herein may be in various forms, such as in the form of liquids, shampoos, creams or gels, or in any other suitable form.

[0249] In one embodiment, the composition is in the form of a lightening dye shampoo comprising a cosmetically acceptable aqueous medium.

[0250] In the composition disclosed herein, when at least one oxidation base is used, optionally in the presence of at least one coupler, or when the at least one fluorescent dye is used in the context of a lightening direct dyeing, then the composition disclosed herein may also comprise at least one oxidizing agent.

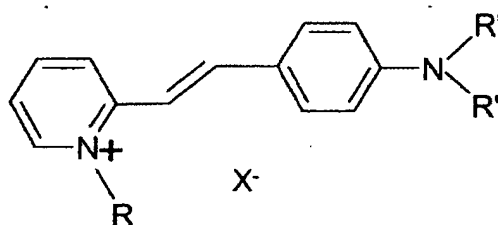
[0251] The at least one oxidizing agent may be chosen, for example, from hydrogen peroxide, urea peroxide, alkali metal bromates, persalts such as perborates and persulphates, and enzymes such as peroxidases and two-electron or four-electron oxidoreductases. In one embodiment, the at least one oxidizing agent is chosen from hydrogen peroxide and enzymes.

[0252] Further disclosed herein is the use of a composition for dyeing a human keratin material with a lightening effect, comprising, in a cosmetically acceptable medium, at least one fluorescent dye that is soluble in the medium and at least one associative polymer chosen from associative polyurethane derivatives, associative cellulose derivatives, associative polyvinylactam derivatives and associative unsaturated polyacid derivatives.

[0253] In the context of this use, the at least one fluorescent dye may be chosen from the fluorescent dyes belonging to the following families: naphthalimides; cationic and non-cationic coumarins; xanthenodiquinolizines (such as sulphorhodamines); azaxanthenes; naphtholactams; azlactones; oxazines; thiazines; dioxazines; monocationic or polycationic fluorescent dyes of azo, azomethine and methine types, alone or as mixtures.

[0254] For example, the compounds of formulae F1, F2 and F3 already described may be used.

[0255] It is similarly possible to use the compounds of formula (F4) below:



wherein R is chosen from methyl and ethyl radicals; R' is a methyl radical and X<sup>-</sup> is an anion chosen, for example, from chloride, iodide, sulphate, methosulphate, acetate and perchlorate. An example of a compound of this type that may be mentioned is the Photosensitizing Dye NK-557 sold by the company Ubichem, wherein R is an ethyl radical, R' is a methyl radical and X<sup>-</sup> is an iodide.

[0256] Everything that has been described previously regarding the natures and contents of the various additives present in the composition remains valid and will not be repeated in this section.

[0257] As used herein, the term “human keratin materials” includes the skin, the hair, the nails, the eyelashes and the eyebrows, such as dark skin and artificially colored or pigmented hair.

[0258] Further as used herein, the term “dark skin” means a skin whose lightness  $L^*$  measured in the CIEL  $L^*a^*b^*$  system is less than or equal to 45, such as less than or equal to 40, given that  $L^*=0$  is equivalent to black and  $L^*=100$  is equivalent to white. The skin types corresponding to this lightness are, for example, African skin, afro-American skin, hispano-American skin, Indian skin and North African skin.

[0259] As used herein, the term “artificially dyed or pigmented hair” means hair whose tone height is less than or equal to 6 (dark blond) such as less than or equal to 4 (chestnut-brown).

[0260] The lightening of the hair is evaluated by the “tone height”, which characterizes the degree or level of lightening. The notion of “tone” is based on the classification of the natural shades, one tone separating each shade from the shade immediately following or preceding it. This definition and the classification of the natural shades are well known to hairstyling professionals and are published in the book “Sciences des traitements capillaires [Hair treatment sciences]” by Charles Zviak, 1988, published by Masson, pp. 215 and 278.

[0261] The tone heights range from 1 (black) to 10 (light blond), one unit corresponding to one tone; the higher the figure, the lighter the shade.

[0262] Further disclosed herein is a process for dyeing human keratin fibers with a lightening effect, comprising:

- a) applying to the keratin fibers a composition disclosed herein for a time that is sufficient to develop the desired coloration and lightening,
- b) optionally rinsing the keratin fibers,
- c) optionally washing the keratin fibers with shampoo and optionally rinsing the keratin fibers,
- d) drying the keratin fibres or leaving the keratin fibers to dry.

[0263] Also disclosed herein is a process for coloring dark skin with a lightening effect, comprising applying to the skin a composition disclosed herein and drying the skin leaving the skin to dry.

[0264] Everything that has been described previously regarding the various constituent components of the composition remains valid, and reference may be made thereto.

[0265] For example, the processes disclosed herein are suitable for treating human keratin fibers, such as artificially colored and pigmented hair, or dark skin.

[0266] In one embodiment, the keratin fibers that may be treated with the process as disclosed herein have a tone height of less than or equal to 6 (dark blond) such as less than or equal to 4 (chestnut-brown).

[0267] Furthermore, a dark skin capable of being treated in accordance with the disclosure has a lightness  $L^*$ , measured in the CIEL  $L^*a^*b^*$  system, of less than or equal to 45 such as less than or equal to 40.

[0268] In a first embodiment, the process of dyeing fibers with a lightening effect is performed with a composition that does not comprise any oxidation dyes or coupler and in the absence of oxidizing agent.

[0269] In a second embodiment, the process of dyeing fibers with a lightening effect is performed with a composition that does not comprise any oxidation dyes or coupler, but in the presence of at least one oxidizing agent.

[0270] According to one embodiment of the dyeing process disclosed herein, at least one composition as defined above is applied to the keratin fibers, such as the hair, for a time that is sufficient to develop the desired coloration and lightening, after which the fibers are rinsed, optionally washed with shampoo, rinsed again and dried.

[0271] According to a second embodiment of the dyeing process disclosed herein, at least one composition as defined above is applied to the keratin fibers, such as the hair, without final rinsing.

[0272] According to a third embodiment of the dyeing process disclosed herein, the dyeing process comprises a preliminary operation comprising separately storing, on the one hand, a composition disclosed herein comprising, in addition to the at least one fluorescent dye and the at least one associative polymer, optionally at least one oxidation base and/or at least one coupler, and, on the other hand, a composition comprising, in a cosmetically acceptable medium, at least one oxidizing agent, then mixing them together at the time of use, and applying to the keratin fibers, such as the hair, the mixture for a time that is sufficient to develop the desired coloration, rinsing the keratin fibers, optionally washing the keratin fibers with shampoo, rinsing again and drying the keratin fibers.

[0273] The time required to develop the coloration and to obtain the lightening effect on the keratin fibers, such as the hair, may range from 5 to 60 minutes, such as from 5 to 40 minutes.

[0274] The temperature required to develop the coloration and to obtain the lightening effect may range from room temperature (15 to 25°C) to 80°C, such as from 15 to 40°C.

[0275] Also disclosed herein is a multi-compartment device for dyeing keratin fibers, such as the hair, with a lightening effect, comprising at least one compartment comprising a composition disclosed herein, and at least one other compartment comprising a composition comprising at least one oxidizing agent. This device may be equipped with a means for applying the desired mixture to the keratin fibers, such as the devices described in French Patent No. 2 586 913.

[0276] It should be noted that the composition disclosed herein, if used to treat keratin fibers, such as chestnut-brown hair, makes it possible to achieve the following results:

[0277] If the reflectance of the hair is measured when it is irradiated with visible light in the wavelength range from 400 to 700 nanometers, and if the curves of reflectance as a function of the wavelength are compared for hair treated with the composition disclosed herein and untreated hair, it is found that the reflectance curve corresponding to the treated hair, in a wavelength range from 500 to 700 nanometers, is higher than that corresponding to the untreated hair.

[0278] This means that, in the wavelength range from 500 to 700 nanometers, such as from 540 to 700 nanometers, there is at least one range in which the reflectance curve corresponding to the treated hair is higher than the reflectance curve corresponding to the

untreated hair. The term “higher than” means a difference of at least 0.05%, such as a difference of at least 0.1% of reflectance.

[0279] However, there may be, within the wavelength range from 500 to 700 nanometers such as from 540 to 700 nanometers, one or more ranges in which the reflectance curve corresponding to the treated fibers is either superimposable on or lower than the reflectance curve corresponding to the untreated fibers.

[0280] In one embodiment, the wavelength at which the difference is maximal between the reflectance curve for the treated hair and that for the untreated hair is in the wavelength range from 500 to 650 nanometers such as in the wavelength range from 550 to 620 nanometers.

[0281] In addition, the composition disclosed herein is, for example, capable of lightening the hair and the skin in a shade which, measured in the CIEL  $L^*a^*b^*$  system, has a variable  $b^*$  of greater than or equal to 6, with a  $b^*/\text{absolute value of } a^*$  ratio of greater than 1.2 according to the selection test described below.

#### Selection test

[0282] The composition is applied to chestnut-brown keratin fibers, such as the hair, at a rate of 10 grams of composition per 1 gram of chestnut-brown fibers. The composition is spread on so as to cover all of the fibers. The composition is left to act for 20 minutes at room temperature (20 to 25°C). The fibers are then rinsed with water and then washed with a shampoo based on lauryl ether sulphate. They are then dried. The spectrophotometric characteristics of the fibers are then measured in order to determine the  $L^*a^*b^*$  coordinates.

[0283] In the CIEL  $L^*a^*b^*$  system,  $a^*$  and  $b^*$  indicate two color axes:  $a^*$  indicates the green/red color axis ( $+a^*$  is red,  $-a^*$  is green) and  $b^*$  indicates the blue/



yellow color axis (+b\* is yellow and -b\* is blue); values close to zero for a\* and b\* correspond to grey shades.

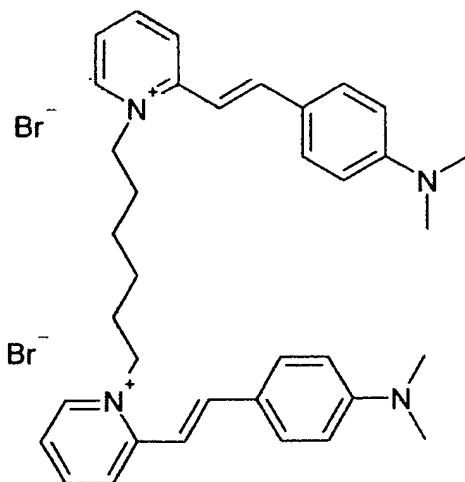
[0284] Other than in the examples, or where otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should be construed in light of the number of significant digits and ordinary rounding approaches.

[0285] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

[0286] The examples that follow are intended to illustrate the disclosure without, however, limiting its scope.

## EXAMPLES

### Fluorescent compound



[0287] 93 g of 2-picoline were reacted with 120 g of 1,6-dibromohexane in dimethylformamide at 110°C for 5 hours.

[0288] The precipitated product was recovered and filtered off.

[0289] 109 g of the product obtained above were dissolved in methanol and 82.82 g of p-dimethylaminobenzaldehyde were added in two portions, in the presence of pyrrolidine.

[0290] The mixture was then left for 30 minutes.

[0291] The product was recovered in precipitated form.

[0292] Analysis by mass spectroscopy: 266.

[0293] Elemental analysis: C: 62.43%; H: 6.40%; Br: 23.07%; N: 8.09%.

[0294] The formula is as follows: C<sub>36</sub>H<sub>44</sub>N<sub>4</sub>·2Br.

### **Compositions**

Composition	1	2
Fluorescent compound	1%	1%
Aculyn 44 (*)	0.5%	-
Styleze W20 (**)	-	0.5%

Distilled water	qs 100%	qs 100%
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[0295] The percentages are expressed by weight of active material.

(\*) associative polyurethane derivative

(\*\*) associative polyvinylactam derivative

**Coloration**

[0296] The compositions were each applied to a lock of natural chestnut-brown hair (tone height 4) with a leave-in time of 20 minutes.

[0297] The locks were then rinsed and dried under a hood for 30 minutes.

[0298] A marked lightening effect was observed on the locks.